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14. ABSTRACT

Soot in engines is present in a rich premixed flame near the fuel injector followed by a diffusion flame where it is burned out. To mimic this structure we perturbed an atmospheric-pressure ethylene diffusion flame by progressively adding oxygen in the fuel stream, while holding constant peak temperature and stoichiometric mixture fraction. The resulting partially premixed flames presented a well-defined double structure, with a (lightly) sooting region sandwiched between a premixed flame component and a diffusion flame one, both flames being coupled thermally and chemically. Such flames were systematically studied by measuring temperature, species

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Major Goals: Objective: Examining onset of soot in counterflow laminar systems in regimes of relevance to compression ignition engines.

Approach: 1) Define well-controlled testbeds that retain some of the challenges of engines (e.g., partial premixing, low temperature combustion, high pressure) but are still well suited to quantitative diagnostics; 2) Study soot inception by measuring gaseous soot precursors and focusing on the gas-to-particle transition.

Relevance to Army: Shedding light on the fundamentals of soot inception in different combustion regimes of direct relevance to engines will result in strategies to reduce engine emissions.

Accomplishments: See uploaded document

Training Opportunities: The following personnel was trained under ARO support: graduate student Francesco Cattaneo, Visiting Assistant in Research in 2014-2015; graduate student Kevin Gleason, Ph.D. Student (2015-Present); Research Associate Francesco Carbone (2014-2017). By the way of professional development they participated in conferences, as listed in another section of the report, while Gleason attended the Combustion Summer School in Princeton for two years in a row. Training entailed direct supervision by the PI and internal seminars or presentations at group meetings.

Results Dissemination: The usual vehicles of dissemination included peer-reviewed publications (1-5) and conference presentations (6-11) as listed below:
1. F. Carbone, F. Cattaneo, A. Gomez., Combustion and Flame 162 (2015) 4138-4148.
2. F. Carbone, K. Gleason, A. Gomez., Proc. Combust. Inst. 36 (2017) 1395-1402.
3. F. Carbone, M. Attoui, A. Gomez., Aerosol Science and Technology 50 (2016) 740-757.
4. F. Carbone, K. Gleason, A. Gomez, Combustion and Flame 181 (2017) 315-328.
5. F. Carbone, S. Moslih, A. Gomez, Combustion and Flame 181 (2017) 329-341.
6. F. Carbone, S. Moslih, M. Attoui, A. Gomez, Gas-to-particle transition in a moderately sooting laminar C2H4/air premixed flame, 9th U. S. National Combustion Meeting, Cincinnati, Ohio, May 17-19, 2015.
7. F. Cattaneo, F. Carbone, A. Gomez, Structure of incipiently sooting partially premixed counterflow ethylene flames, 9th U. S. National Combustion Meeting, Cincinnati, Ohio, May 17-19, 2015.
8. K. Gleason, F. Carbone, A. Gomez, Pressure Effects on Incipiently Sooting Partially Premixed Counterflow Flames of Ethylene, 2016 Spring Technical Meeting of the Eastern States Section of the Combustion Institute, Princeton, New Jersey, March 20-22, 2016.
9. F. Carbone, M. Attoui, A. Gomez, Differential mobility analysis of soot nuclei in a laminar C2H4/air premixed flame, Aerosol Technology 2015, Tampere, Finland, June 15-17, 2015.
10. F. Carbone, M. Attoui, A. Gomez, High Resolution Differential Mobility Analysis of Nascent Soot in a Laminar Premixed Flame, Aerosol Reaction Engineering, Center for Aerosol science and Engineering (CASE) Workshop 2016, Saint Louis, Missouri, May 24-25, 2016;
11. F. Carbone, A. Gomez, "Thermophoresis and Differential Mobility Analysis of soot nuclei sampled from a premixed flame," presented at the American Association for Aerosol Research (AAAR) 35th Annual Conference. Portland, Oregon, October 17-21, 2016.

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 Other Collaborators:

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Paper Title: Pressure Effects on Incipiently Sooting Partially Premixed Counterflow Flames of Ethylene
Authors: Kevin Gleason, Francesco Carbone, Alessandro Gomez
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1. Introduction- <u>Realizing Engine-Relevant Conditions in Bench-Top Laboratory Systems</u>

The practical control of pollutant formation and emission involves careful design of the engine and of the fuel injection, and is generally engine-specific. Establishing conditions of direct relevance to engines but in more convenient and well-defined settings would benefit our understanding of the fundamentals of the process and ultimately lead to the design of better engines. Even when equipped with optical access, engines do not lend themselves to detailed probing and the quantitative implementation of diagnostic techniques that are routinely used in bench-top laboratory flames. As a result, it is difficult to progress experimentally beyond a qualitative understanding in these environments.

Realizing engine conditions in bench top laboratory systems is useful so long as key ingredients of relevance to engines are retained by covering appropriate ranges of equivalence ratio, temperature, pressure, composition (including Exhaust Gas Recirculation (EGR)) and turbulence. Of course, some of these key matching features will have to be sacrificed on the altar of simplification. In particular, to be able to focus on a chemical kinetic characterization of these flames/reactors, we need to remove the fluid mechanic indeterminacy associated with turbulence, and the time-dependence of the engine behavior associated with in cylinder compression/expansion, which significantly alters the thermodynamic environment in which combustion takes place. This need is motivated by the fact that a detailed chemical characterization of the combustion environments necessarily relies on analytical chemistry tools that are incompatible with highly time-dependent, let alone turbulent, phenomena. Therefore, steady laminar environments with simple fluid mechanics and complex kinetics are favored. Achieving high pressure at the level of relevance to engines, on the order of several MPa requires a fairly compact system to keep cost manageable and size of the apparatus within the spatial constraints of an instrumented bench top. As to the combustion regimes of relevance to Compression Ignition (CI) engines, they include *diffusion flames and Partially Premixed Flames (PPFs),* with an appropriate selection of composition, temperature and pressure levels to establish engine-relevant conditions.

The *diffusion flame* is the configuration that is traditionally associated with a CI engine and does not require any further discussion. Its adaptation to high-pressure conditions is best achieved in the *counterflow* configuration for reasons explained in our previous work: namely, the characteristic length scale over which buoyancy acts is shorter than in coaxial flames and the corresponding Richardson number that scales with the third power of this length scale is much smaller in counteflow than in coflow. As a result, buoyancy instabilities are not an issue, as we demonstrated in detailed measurements up to 3 MPa [1-2].

The conceptual picture of CI engines has changed over the years and there is merit in considering also PPFs. Research discussed in [3-4] showed that vaporization and mixing occur reasonably fast and rich premixed combustion is established in the vicinity of the injector with the initial soot loading generated in this regime. Subsequently, soot grows and is oxidized further downstream across an envelope diffusion flame that is formed between the products of the rich premixed flame and the oxidizer. To mimic this situation, a counterflow *laminar* configuration is also ideal. The analogy between the schematic representation in compression ignition engines, adapted from [4], and the counterflow partially premixed flame is shown in Fig. 1. In the same spirit as the flamelet approach to turbulent combustion, we de facto "unfold" the complex flame structure of an in-cylinder locally sooting engine into this double flame structure, consisting of a rich partially premixed flame back supported by the diffusion flame established between unburned combustion products, e.g., mostly CO and H_2, and the counterflowing oxidizer stream.
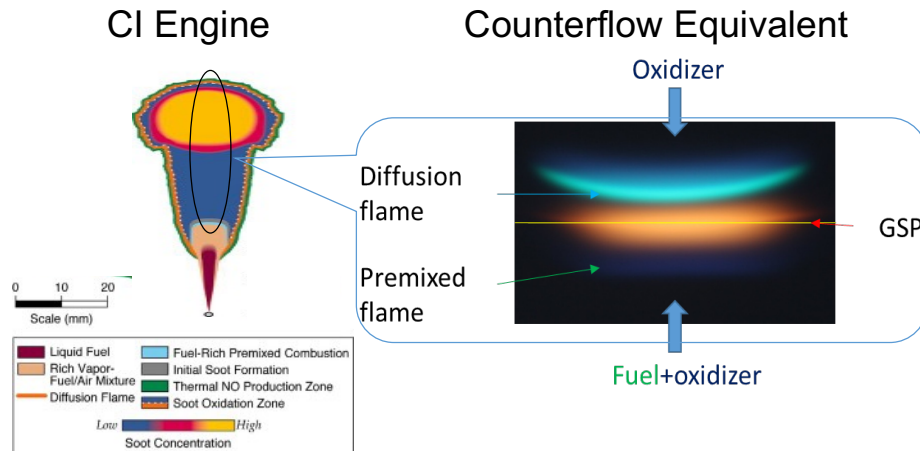
CI Engine **Counterflow Equivalent**

Figure 1: Analogy between the CI engine combustion scenario [4] and a typical partially premixed flame in the present study.

2. Major Accomplishments

The structure of partially premixed incipiently sooting flames at pressures up to 0.8 MPa was systematically studied by measuring temperature, species concentrations up to 3-ring aromatics and soot volume fraction for subsequent comparison with simple, mostly one-dimensional, computational modeling with well-specified boundary conditions, using detailed chemical kinetics, including soot precursors. The two most significant innovations in the study include: a) a remarkable control of the *temperature-time history* to soot, which evidences unequivocally cause-effect relationships in the path to soot formation and its dependence on peak temperature and pressure and b) the application of a criterion for accurate gas sampling from these flames for subsequent Gas Chromatograph and Mass Spectrometer (GC/MS) analysis. For the latter the use of microprobes scaled on the basis of the pressure-dependent flame thickness and corrections to the species profile to account for minor displacements of the flame position caused by the insertion of the probe were critical to ensure good agreement between experiments and models of major products and some critical species like benzene. In a parallel investigation we also examined details of the soot nucleation process with novel diagnostics in premixed flames for eventual adaptation to the counterflow configuration. The results of this highly productive effort are five peer-reviewed articles [5-10], at least one additional article in preparation with a focus on soot volume fraction measurements, and several presentations at the US meetings of the Combustion Institute [11-12] and aerosol conferences [13-15]. We review briefly key findings with further details available in the listed references.

We provide first a glimpse of the level of control we exercised on these flames. We started off by perturbing an ethylene diffusion flame, progressively adding oxygen in the fuel stream, while holding constant peak temperature and stoichiometric mixture fraction [5]. The resulting partially premixed flames presented a well-defined double structure [16], with a (lightly) sooting region sandwiched between a premixed flame component and a diffusion flame one, both flames being coupled thermally and chemically. The picture on the right in Fig. 1 shows one such flames at Φ=3 and atmospheric pressure. There have been several studies on soot

formation in PPFs [e.g.,17-20], but without the control of the temperature-time history that we exercised in this study.

As a first step to approach engine conditions, we raised the pressure in these flames to 0.8 MPa to examine its effect on the flame structure [6]. Figure 2 shows pictures of the flames that invariably become sootier as the equivalence ratio was lowered (left-to-right in Fig. 2). As pointed out in [5], different trends would be observed by using air as an oxidizer, as in previous studies on partially premixed flames [18-19]. Figure 3 shows the computed temperature versus the convective residence time for all flames. The residence time is calculated by integration of the inverse of the axial velocity component al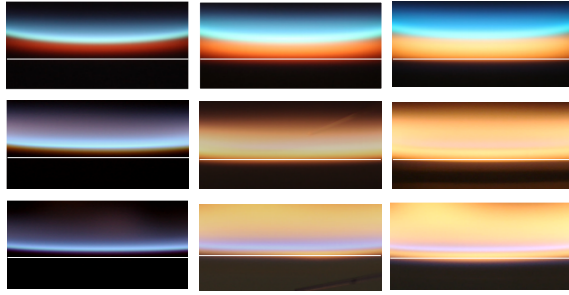ong the burner axis. The graph is interrupted in the vicinity of the gas stagnation plane where the vertical dashed line is located since, by definition, the residence time diverges at that location. Maintaining conditions of incipient sooting as the pressure was raised required that the peak temperature be lowered by inert dilution. Symbols on a given curve bracket the soot forming region marked by arrows in Fig. 4 and appearing at temperatures above 1400K-1475K. The diffusion flames exhibit soot in a very narrow region near the diffusion flame side. As the equivalence ratio is lowered, the soot-laden region broadens, reaches the gas

Figure 2. Images of the nine flames with a horizontal line marking the gas stagnation plane. Top to bottom: P=0.1, P=0.4 and P=0.8 MPa, respectively. Left to right: Φ=∞, Φ=6.5 and Φ=5, respectively.

stagnation plane and extends to the premixed side of the gas stagnation plane. Furthermore, the temperature range within which soot is present is lowered at constant composition as the pressure is raised and yet the soot load seems to increase on the basis of the visual appearance of the flame as a result of the pressure increase. In this study the temperature necessarily varies from flames to flame, but there is still a partial similitude that enables us to retain a level of control: if we replot these figures by nondimensionalizing the temperature with the peak value, all profiles (solid lines) collapse showing that the *normalized* temperature-convective time history remains nearly constant while the pressure is varied (see middle plots in Fig. 3). Therefore, temperature, along with pressure, is evidenced as a key controlling parameter, which is expected in the high activation energy processes leading to soot formation. At a fixed pressure, lowering the equivalence ratio by increasing the level of premixedness increases the temperature value in the region straddling the stagnation plane. As a result, soot formation is enhanced since the pyrolytic growth reactions occurring in proximity of the stagnation plane are boosted by the temperature increase [6], which confirms our findings at atmospheric pressure [5].

Accounting for the convective time is only part of the story, but one should consider also the effect of pressure on transport. Another way of rescaling the problem is offered by a normalization of the axial coordinate, z, with respect to a diffusion length $\delta \approx \sqrt{D/a}$, as discussed in previous work in our group [2, 6]. Since the strain rate is kept constant in all of these flames as the pressure is changed, one has to take into account the change in the diffusion
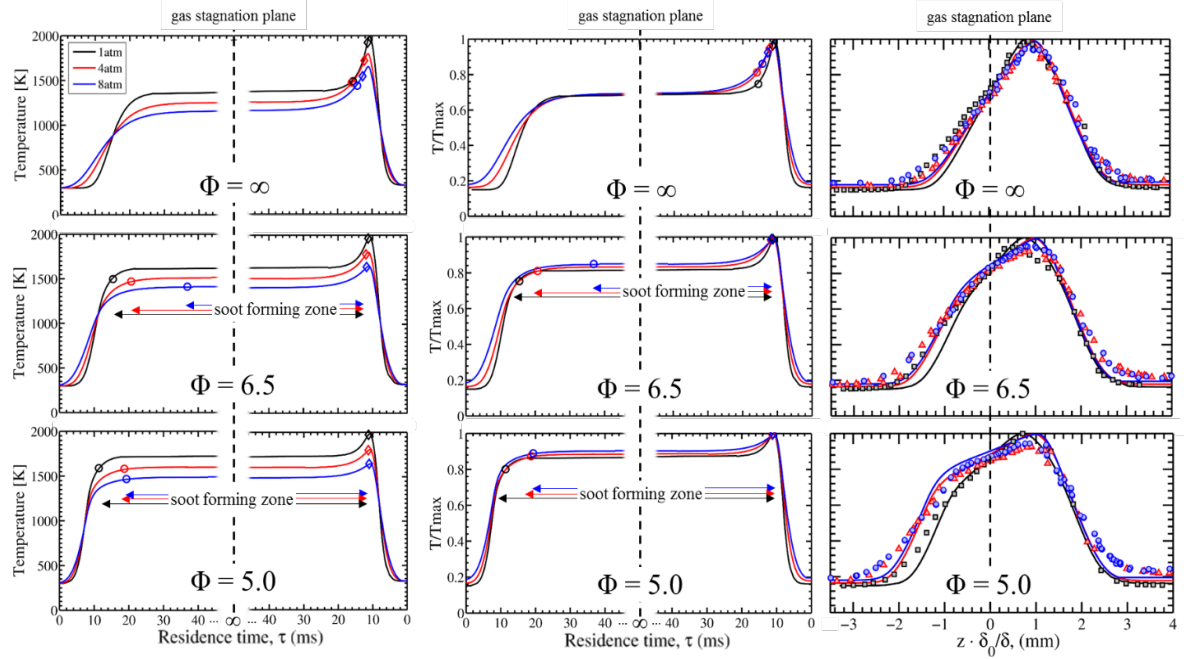
Figure 3. Plots are color coded in black for P=0.1 MPa, red for P=0.4 MPa and blue for P=0.8 MPa. Left panels: computed temperature versus convective time. Middle panels: computed temperature normalized with respect to T_{max} that is approximately 1986 K, 1810 K, and 1650 K for all mixtures in order of increasing pressure. Symbols superimposed on the curves bracket the soot laden zone. A break in the curves is present near the gas stagnation planes (vertical dashed line) where the abscissa diverges by definition; the premixed flame side is on the left and the diffusion flame side on the right of the gas stagnation plane. Right panels: normalized temperature versus axial coordinate rescaled with respect to a pressure-dependent diffusion length.

length through the pressure-dependence of the diffusivity. Accordingly, $\delta \approx \sqrt{(p \cdot a)}$ and if we choose the atmospheric pressure for reference, a pressure change will result in a rescaled

diffusion length as $\frac{\delta}{\delta_0} = \sqrt{\frac{D_0}{D}} \approx \sqrt{\frac{P_0}{P}}$, where the subscript refers to atmospheric pressure conditions. Therefore, when the axial coordinate is rescaled by dividing it by this nondimensional diffusion length, profiles at a given equivalence ratio should collapse regardless of pressure. Indeed, they do in the case of the diffusion flames, as shown in the top rightmost panels in Fig. 4. The scaling applies reasonably well also for partially premixed flames because the laminar propagation velocity of the fuel mixture was purposely lowered through inert dilution when the pressure was increased. Therefore, the process of lowering the peak temperature as pressure was raised, that was initially motivated by the need to keep soot loading at modest levels compatibly with gas microsampling, yields the most desirable scenario for a fair comparison among partially premixed flames at different pressures. The selected flames realize very similar temperature-time histories in both convective and diffusive terms so that pressure and peak temperature emerge as main controlling factors.

For a proper comparison of experiments and model, an accurate determination of the velocity boundary conditions at the burner nozzle outlets is critical for it to be used in detailed one-dimensional modelling. It was achieved by two-dimensional axisymmetric modelling of the purely diffusive flames at different pressures [9]. The two-dimensional model was implemented in the COMSOL Multiphysics (Comsol Inc.) finite element solver package and used simplified chemistry to reproduce the measured flame temperature profile. It includes the flow in the burner nozzles and shroud housing to allow for accurate prediction of the velocity

profiles at the nozzle outlets. The boundary conditions were used subsequently for detailed-chemistry one-dimensional modelling.

Details of the more than 20 detected species profiles are provided in [9-10]. Here for brevity we provide a sample of the type of comparison using benzene as a critical soot precursor. Figure 4 shows a comparison between measured and computed mole fractions for both diffusion flames and partially premixed flames at 0.1, 0.4 and 0.8 MPa. The agreement between experiments and model, using USC-MechII chemistry, at all compositions and pressures is quite good for this species that is regarded as a bottleneck to soot, which enabled us to pursue a reaction path analysis, as detailed in [10].

Principal conclusions of this study are as follows:

a) at a fixed pressure, partial premixing increases the temperature value in the region straddling the stagnation plane. As a result, benzene formation is enhanced because the oxidative pyrolysis reactions occurring in proximity of the stagnation plane are boosted by the temperature increase.

b) At a fixed equivalence ratio, increasing the pressure results in higher benzene mole (soot volume) fractions under partially premixed conditions despite the decrease in peak temperature caused by additional inert dilution. Pressure effects and a reduction in the concentration of oxidizing species like OH back-diffusing from the diffusion flame part of the PPF more than compensate for the decrease in peak temperature.

c) As pressure increases, the C2/C4 path contributes more and more to benzene formation by comparison with the C3 alternative.
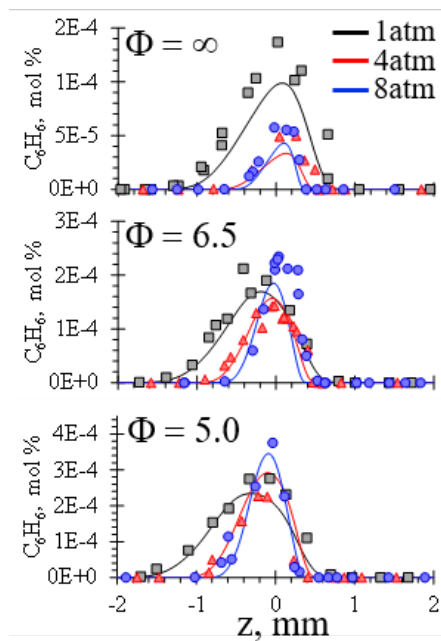

Figure 4. Spatial profiles of benzene mole fractions as a function of distance from the stagnation plane. Solid lines show results with the USC-II model.

To complete the database for subsequent modeling, it is important to gather quantitative measurements of soot. The traditional extinction measurements are not well suited to this type of flames because of the modest soot loading and short absorption path length. Consequently, we resorted to multicolor pyrometry. Flame images were recorded using a digital camera with a well characterized spectral response [25]. The color filter array was separated into individual red, green, and blue channels and each channel provided a two-dimensional projection of the signals upon Abel inversion. Temperature profiles were inferred from the ratio of any two color channels relating soot temperature to the intensity of radiation emitted by soot whose emissivity decays with a power law of the wavelength ($\varepsilon \propto \lambda^{-\alpha}$). Using a thermocouple as an absolute emission calibration [26] and for independent measurements of the gas temperature, soot volume fraction and emissivity dispersion index, α, were also determined with the method reported in [8]. We performed soot measurements in several flames at various peak temperatures and at P=0.1 MPa, P=0.4 MPa, and P=0.8 MPa. Figure 5 shows soot volume fraction and computed benzene concentration profiles as a function of normalized axial coordinate. We used the *computed* benzene profiles in the light of the validation provided by Fig. 4, since for several of these flames the relatively large soot load prevented microprobe gas sampling. We notice that the soot volume fraction invariably increases with peak temperature and pressure both in the

diffusion flames and partially premixed flames. This behavior is mirrored also by the trends in computed benzene profiles. As mentioned earlier, at a fixed pressure and peak temperature, partial premixing enhance benzene and soot formation because of the increased temperature in the soot forming region, enhancing pyrolytic growth reactions.
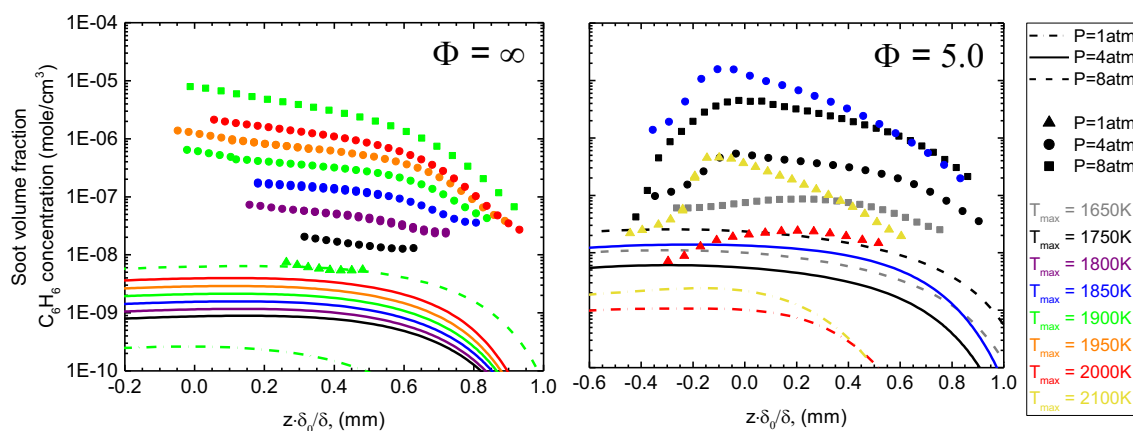

Figure 5. Measured soot volume fraction (symbols) and computed benzene concentration (lines) for diffusion flames (left) and partially premixed flames (right) *vs.* axial coordinate, z, normalized with respect to the diffusion length (see Fig. 3 discussion). Legend for symbols, lines and color in rightmost panel.

The database with the measurements of critical soot precursors up to 3-ring aromatics is available online to modelers to improve the chemical reaction mechanism [24]. To give a glimpse of the richness of the database, we show in Fig. 6 an examples of profiles of parent fuel molecule, some critical intermediates as evidenced by reaction path analysis [6] and soot volume fraction of the 0.4 MPa diffusion flame and the $\Phi= 5$ partially premixed one, both with a peak temperature of 1800 K. For clarity of presentation we report only eight of the more than twenty gaseous species that were sampled and analyzed, including: the parent molecule, C_2H_4, acetylene, a critical species on soot formation with respect to both nucleation and surface growth, C_3H_4 that was shown to be an important intermediate to benzene in [6], benzene, arguably the bottle neck to the formation of the soot nuclei, and a few PAHs such as naphthalene (A2), acenaphthylene (A2R5) and methylnaphthalene (A2CH3), in addition to the computed temperature profile and measured soot volume fraction. The origin of the abscissa is at the gas stagnation plane. In the diffusion flame, fuel coming in from the left in the figure is used up at approximately z=0.5 mm, where it is transported by diffusion. Near that location the measured intermediates and soot first appear, with the peak of the intermediate at approximately z=0.2-0.3 mm. Soot, first detected at a temperature of 1700 K grows monotonically as it is transported towards the gas stagnation plane and is last detected at the location where the local temperature is approximately 1360 K. Its first appearance is subsequent to the onset detection of the aromatics.

The challenges of sampling at even moderate pressure such flames is selfevident, with most of the chemical "action" to soot confined to a region on the order of a fraction of millimeter thick. Nevertheless, the peak values of concentration and the sequence in the evolution from smaller molecules at larger concentrations to progressively larger ones at ever smaller concentrations, and eventually soot is captured well and can be object of comparison and validation of models, with the further enrichment by the addition of 14 species detected and not plotted for clarity of presentation. In the partially premixed case on the right, the situation is similar but with a few important differences: the region of intense chemical activity is broader and approximately sandwiched between the diffusion flame component, where the temperature peak is located, and the premixed flame component, where the "kink" in the temperature profile is located,

approximately at z=- 0.5 mm; the soot volume fraction is nonmonotonic, with a contribution from both flame components and its peak value is much larger than in the purely diffusion flame counterpart (left panel).
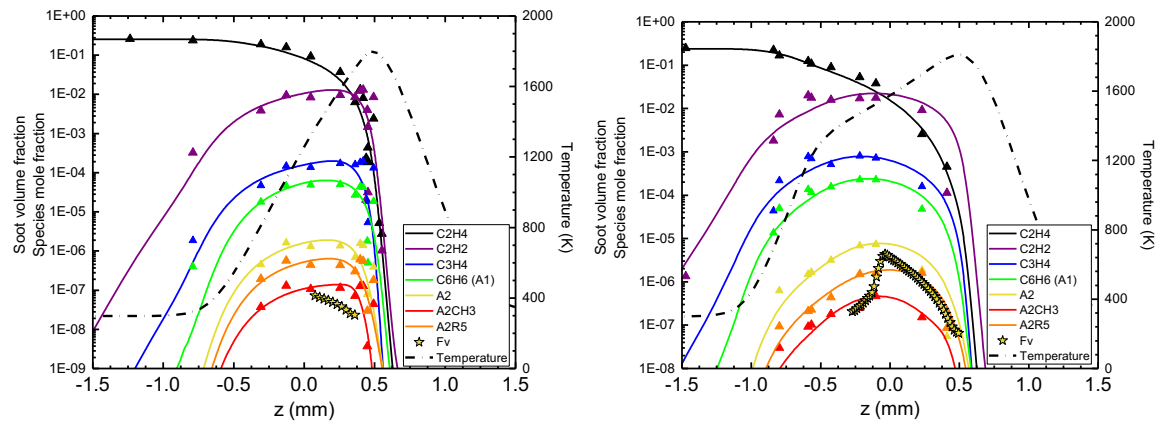

Figure 6. Mole fraction of a subset of gaseous species, computed temperature (dashed line) and measured soot volume fraction of a diffusion flame (left) and =5 partially premixed flame (right) (P= 0.4 MPa and T_{max}= 1800 K). Abscissa origin is at the gas stagnation plane, with fuel injected from the left and oxidizer from the right. Continuous lines are trend lines for guidance; A2, A2R5 and A2CH3 are short for naphthalene, acenaphthalene and methylnaphthalene, respectively.

In a parallel investigation we applied various diagnostics to the measurements of the smallest detectable soot nanoparticles in a flat premixed flame and compared them for selfconsistency [11-13]. We performed measurements in this relatively simple flame, even though it is not directly related to the engine-relevant counterflow configuration of [9-10], since it has been the workhorse for soot research in flames for decades because of its simplicity. As a result, it is a useful testbed to test and optimize diagnostic techniques, such as the multicolor pyrometry and the measurement of the transition from the gas phase to the particle phase [8], before ultimately applying them to the partially premixed flames of interest. To that end, we relied on: a) in situ microsampling followed by GC-MS analysis for the quantification of the gas phase up to 3-ring aromatics; b) soot nanoparticle sampling followed by quick dilution and High-Resolution Differential Mobility Analysis (HR-DMA); c) spatially-resolved Thermophoretic Sampling (TS) followed by microscopy analysis; d) multicolor pyrometry and e) standard laser extinction/scattering. The redundancy of methods may shed light on possible biases and artifacts of the different techniques in the examinations of the gas-to-particle transition. There is general good selfconsistency between TS and HR-DMA data. The HR-DMA data reveal pitfalls in the data in the literature.

As an example, we show the size distributions of nascent soot as detected by the DMA at two different locations in Fig. 7 and compare them with similar data in the literature. Soot nuclei form early in the flame, are smaller than 3 nm and cannot be detected with traditional diagnostics on which literature data are based. The number concentrations inferred by measurements in positive polarity are significantly larger than that in negative polarity (10^{13}-10^{12} cm^{-3}). The size distribution functions of nascent soot appear to be monomodal with sub-3nm sizes for Height Above Burner (HAB) up to 10mm when coagulation in the probe is minimized. It is apparent that the measurements in the literature with a conventional DMA missed out on these nuclei and yet they will be critical to monitor the hitherto poorly understood gas-to-particle transition.
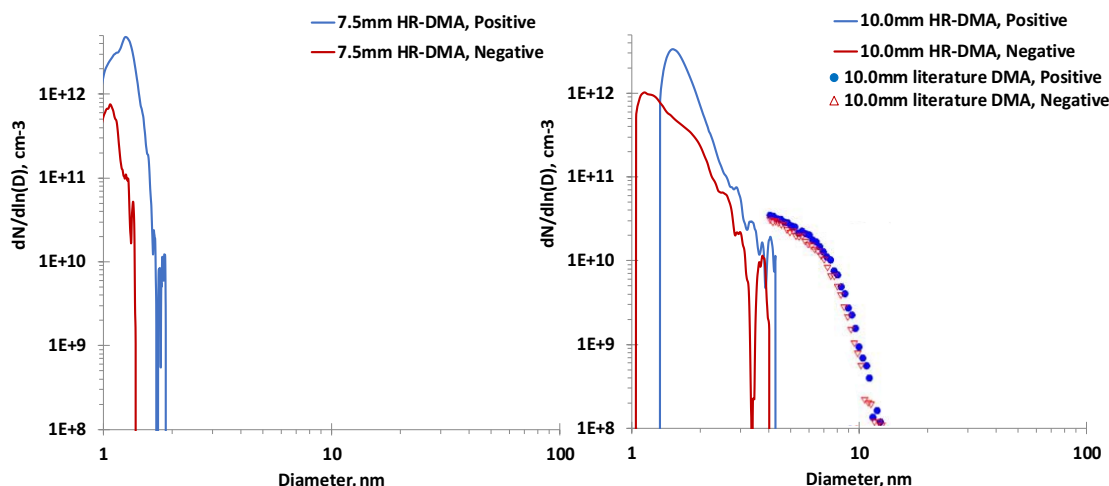
Figure 7. Size distribution functions of soot nanoparticles at two heights in the postflame region of a flat premixed flame.

We completed the "detour" on premixed flames by assessing possible artifacts induced by the presence of the probes and their intrusiveness by three-dimensional modeling of the flow using the COMSOL multiphysics (Comsol Inc.) finite element solver package. We concluded that, without major scale up of the counterflow burner, soot sampling through a high dilution probe for subsequent DMA analysis is much too perturbative for measurements in the counterflow configuration. Further experiments are needed to assess if thermophoretic sampling on fine wires can be adapted to it to complement optical measurements in future work on the soot characterization in our counterflow systems. The developed database encompassing both gas phase and particles phase provides as complete a benchmark for the validation of soot nucleation models.

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